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COMPLETE SPECIFICATION

Lubricant Compositions

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to lubricant compositions comprising one or more lubricants and one or more salts of polyvalent metals and alkylsalicylic acids.

The use of salts of polyvaylent metals and alkylsalicylic acids as lubricant additives is known. The said salts have the property that they, when applied in small amounts in lubricants, ensure that the inside of engine cylinders, in particular diesel engine cylinders, remains clean and that deposition of carbonaceous products on pistons and in piston grooves is counteracted, so that piston-ring sticking is prevented.

Recent developments in the field of diesel engines tend towards higher thermal loads, which leads in particular to an increase in piston temperature in the area of the piston-ring grooves. One of the possibilities of preparing lubricating oils that meet the demands of these present-day engines involves improvement of the aforesaid salts of polyvalent metals and alkylsalicylic acids as regards their dispersancy at high temperature.

It has now been found that lubricant compositions with improved dispersant properties at high temperatures may be prepared by incorporating one or more salts of polyvalent metals and alkylsalicylic acids in a lubricant or mixture of lubricants, if the alkylsalicylic acids from which the metal salts have been derived satisfy these two requirements:

1. They must contain at least one alkyl group with more than 12 carbon atoms.
2. More than 60 %m of the acids must be acids which contain an alkyl group that is attached to the benzene nucleus in para position relative to the hydroxyl group.

The salts of polyvalent metals and alkylsalicylic acids containing an alkyl group with more than 12 carbon atoms as have hitherto been proposed as lubricant additives in the literature have, as far as can be inferred from the mode of preparation stated, all of them been derived from mixtures of alkylsalicylic acids which contain at most about 50%m, but in most cases considerably less than 50%m, of acids wherein an alkyl group occurs that is attached to the benzene nucleus in para position relative to the hydroxyl group.

The invention consequently relates to lubricant compositions comprising one or more lubricants and one or more salts of polyvalent metals and alkylsalicylic acids, which alkylsalicylic acids contain at least one alkyl group with more than 12 carbon atoms and of which more than 60%m consists of acids containing an alkyl group that is attached to the benzene nucleus in para position relative to the hydroxyl group.

During the combustion process inside the engine the sulphur compounds present in the engine fuel may form sulphur trioxide (SO_3), among other things, which is converted into sulphuric acid with the water present in the combustion gases. This sulphuric acid may, inter alia, induce corrosion of metal parts of the engine and is also capable of converting the salts added to the lubricating oil into the corresponding acids, which may likewise have a corrosive action. In order to neutralize the acidic compounds formed in the engine during the combustion process, it is desirable that a neutralizing agent be present in the lubricating oil. It has been found that this desire can be satisfied by employing the afore-

said salts of polyvalent metals and alkylsalicylic acids in the form of basic salts. By the term "a basic salt of a polyvalent metal and an alkylsalicylic acid" as used in the description and claims of this patent application must be understood a compound of a polyvalent metal or a mixture of compounds of polyvalent metals which contains, besides the polyvalent metal, also one or more acid radicals of alkylsalicylic acids and wherein the number of gram equivalents of polyvalent metal is greater than the number of gram equivalents of alkisalicylic acid. The basicity of such salts of polyvalent metals can be expressed in the formula

$$\left(\frac{M}{Z}-1\right)\times 100\%,$$

where M stands for the number of equivalents of polyvalent metal and Z for the number of equivalents of alkylsalicylic acid, for example per 100 grams of the basic metal salt. A basicity of the polyvalent metal salts up to about 250% is in general amply sufficient for the application in question. The use of basic salts with a basicity between 50 and 200% is preferred.

Among the salts of polyvalent metals and alkylsalicylic acids that are suitable for the preparation of the lubricant compositions according to the invention, the salts of divalent metals are particularly eligible. Preference is given to salts of the alkaline earth metals, in particular to calcium salts.

As was already stated, the metal salts that are suitable for the preparation of lubricant compositions with improved high-temperature properties must have been derived from alkylsalicylic acids which contain at least one alkyl group with more than 12 carbon atoms. Preferably, alkylsalicylic acids are chosen which contain at least one alkyl group having 14 to 18 carbon atoms. As regards the molar percentage of the acids containing an alkyl group which is attached to the benzene nucleus in para position relative to the hydroxyl group, it may furthermore be remarked that particular interest attaches to salts of alkylsalicylic acids wherein the said molar percentage is upwards of 70.

Salts of polyvalent metals and alkylsalicylic acids satisfy the requirements stated above may be prepared in various manners. Four methods of preparation which have led to very good products are mentioned hereinafter. This enumeration is by no means limitative, however, because salts of polyvalent metals and alkylsalicyclic acids which have been prepared in a different way are obviously also suitable for the preparation of the lubricant compositions concerned, provided that they satisfy the requirements on structure specified hereinbefore.

The desired salts may be prepared, for instance, starting from phenol, ortho-alkylphenol or para-alkylphenol, by alkylation, carboxylation and salt formation. The alkylating agent preferably chosen is an olefin or a mixture of olefins with more than 12 carbon atoms to the molecule. Acid-activated clays have proved very suitable catalysts for the alkylation of phenol and ortho- and para-alkylphenol. The amount of catalyst employed is in general 1—10%w, in particular 3—7%w, referred to the sum of the amounts by weight of alkylating agent and phenol to be alkylated. The alkylation may be carried out at temperatures between 100 and 250°C, in particular between 125 and 225°C.

If the preparation of the salts by alkylation with olefins starts from phenol, it is preferred to use 2 to 4 mole of olefin per mole of phenol, in particular 2.5 to 3.0 mole of olefin per mole of phenol. If the preparation of the salts by alkylation with olefins starts from ortho- or para-alkylphenol, it is preferred to use 0.5 to 1.0 mole of olefin per mole of ortho- or para-alkylphenol, in particular 0.7 to 0.8 mole of olefin per mole of ortho- or para-alkylphenol. Excellent results may be obtained by choosing ortho- or para-cresol as starting material for the synthesis of the salts via the ortho- or para-alkylphenol route, respectively.

The alkylphenols prepared via the phenol or ortho- or para-alkylphenol route may be converted into the corresponding alkylsalicylic acids by the technique known for this conversion from the literature. An attractive procedure is, for instance, as follows. The alkylphenols are converted with the aid of an alcoholic caustic solution into the corresponding alkylphenates and the latter are treated with CO_2 at about 140°C and a pressure of 10 to 30 atmospheres. From the alkylsalicylates so obtained the alkylsalicylic acids may be liberated with the aid of, for example, 30% sulphuric acid.

Neutral and basic salts of polyvalent metals may likewise be prepared from these alkylsalicylic acids by the methods described in the literature for this conversion. For the preparation of neutral calcium salts the alkylsalicylic acids may, for instance, be converted into the corresponding sodium salts and these may be allowed to react with an equivalent amount of $CaCl_2$.

For the preparation of basic calcium salts with a relatively low basicity, for instance 50%, the alkylsalicylic acids may be treated with 2 equivalents of calcium in the form of $Ca(OH)_2$. For the preparation of basic calcium salts with a high basicity, for instance 200%, the alkylsalicylic acids may be treated with 4 equivalents of calcium in the form of $Ca(OH)_2$ with introduction of 1.6 equivalents of CO_2.

The desired salts may also be prepared starting from salicylic acid, by alkylation and

salt formation. If the preparation takes place in this way, the alkylating agent preferably chosen is again an olefin or a mixture of olefins with more than 12 carbon atoms to the molecule. BF_3 has proved a very suitable catalyst for the alkylation of salicyclic acid. The amount of catalyst employed is in general 1—2 mole per mole of salicylic acid. The alkylation may be carried out at temperatures between 60 and 150°C, in particular between 100 and 140°C.

If the preparation of the salts starts from salicylic acid by alkylation with olefins, it is preferred to use 1.5 to 4.0 mole of olefin per mole of salicylic acid, in particular 2.0 to 3.0 mole of olefin per mole of salicylic acid.

Neutral and basic salts of polyvalent metals may be prepared from these alkylsalicylic acids by the methods described in the literature for this conversion, just as in the case of alkylsalicylic acids prepared via the phenol and ortho-alkylphenol routes.

The lubricants that are applicable to the preparation of the lubricant compositions according to the invention may be mineral lubricating oils of varying viscosities, but also synthetic lubricating oils or lubricating oils containing fatty oils. The lubricant additives in question can also be incorporated in lubricant greases. The invention is of particular interest for the improvement of the quality of mineral lubricating oils or mixtures thereof. The salts of polyvalent metals and alkylsalicylic acids may be added to the lubricant either as such or in the form of a concentrate obtained, for instance, by mixing the salts with a small amount of oil. The concentration of the metal salts concerned in the lubricants may vary within wide limits. In general, the desired dispersancy is achieved if the lubricants contain 0.01 to 5%w, in particular 0.1 to 1.0%w, of polyvalent metal in the form of the salts in question of polyvalent metals and alkylsalicylic acids. Besides salts of polyvalent metals and alkylsalicylic acids, the lubricant compositions according to the invention may contain still other additives such as antioxidants, foam inhibitors, corrosion inhibitors, means for improvement of the viscosity and/or the viscosity index, means for improvement of the lubricant action and other substances which it is general practice to add to lubricants.

The invention will now be elucidated with the aid of the following examples.

Eleven model substances of the following composition were prepared:

1. calcium salt of 3-cetyl - methylsalicylic acid; basicity 0%
2. " " " " " " " " 26%
3. " " " " " " " " 37%
4. " " " 3-cetylsalicylic acid; " 40%
5. " " " 5-cetylsalicylic acid; " 0%
6. " " " 3,5- dicetylsalicylic acid; " 28%
7. " " " 3,5-dicetyl-4-hydroxybenzoic acid; basicity 25%
8. " " " a mixture of mono- and dicetylsalicylic acids consisting of 18%m of 3-cetylsalicylic acid, 46%m of 5-cetylsalicylic acid and 36%m of 3,5-dicetylsalicylic acid; basicity 54%
9. calcium salt of 3-dodecyl-5-methylsalicylic acid; basicity 44%
10. " " " 3-docosyl-5- " " " 35%
11. " " " 3,5-dioctylsalicylic acid; " 37%

The engine performance of these eleven compounds was investigaged by subjecting the compounds at a concentration of 0.15%w of calcium in a mineral lubricating oil to a short-duration high temperature test (lubricant compositions 1 — 11). The test conditions were as follows:

Engine	Single-cylinder four-stroke diesel engine cooled with ethylene glycol, bore 5 1/8 inches; stroke 6½ inches
Speed	1800 r.p.m.
Load	45 hp
Cooling liquid temperature	85 °C.
Oil temperature	95 °C.
Intake air temperature	45 °C.
Intake air pressure	1340 mm Hg absolute
Amount of lubricating oil tested	5000 g
Fuel	gas oil containing about 1%w of sulphur
Test duration	48 hours

In this test the degree of piston fouling is measured.

For comparison a lubricating oil composition was prepared from the same lubricating oil which again contained 0.15%w of calcium in the form of calcium alkyl salicylate. This calcium alkyl salicylate had, however, been derived from a mixture of C_{14}—C_{18} alkylsalicylic acids prepared on an industrial scale in which about 50%m consisted of acids having an alkyl group attached to the benzene nucleus in para position relative to the hydroxyl group. This calcium alkylsalicylate had a basicity of 50%. Side by side with each engine test for the aforesaid eleven lubricating oil compositions, an engine test with the reference oil was carried out. The results of these engine tests have been collected in Table I. The lubricating oil compositions 4, 7, 9 and 11 do not fall within the purview of the invention. The other ones are compositions according to the invention. In the engine tests a difference in rating was only considered significant if it was 0.3 or more.

TABLE I

Piston Fouling (10 = clean)

Lubricant composition No.	Degree of piston fouling of compositions 1 — 11	Degree of piston fouling of reference oil	Improvement relative to reference oil
1	8.1	7.2	+ 0.9
2	8.2	7.2	+ 1.0
3	8.1	7.4	+ 0.7
4	7.5	7.3	+ 0.2
5	8.0	7.2	+ 0.8
6	7.9	7.0	+ 0.9
7	6.3	7.3	— 1.0
8	8.0	7.0	+ 1.0
9	7.3	7.8	— 0.5
10	8.0	7.2	+ 0.8
11	6.7	7.3	— 0.6

Subsequently a number of calcium salts of alkylsalicylic acids were prepared, starting from salicylic acid. ortho-cresol, para-cresol and phenol. The preparation and composition of the salts are briefly outlined below.

(1) *Starting from salicylic acid*

Salicylic acid was alkylated at 120°C with a mixture of C_{14}—C_{18} olefins (molar ratio 1:2.5), with BF_3 as catalyst (1.5 mole of BF_3 per mole of salicylic acid). In this operation 1 mole of salicylic acid yielded 0.73 mole of alkylsalicylic acids of the following composition:

18%m 3-(C_{14} — C_{18})alkylsalicylic acid

46%m 5-(C_{14} — C_{18})alkylsalicylic acid

36%m 3,5-di(C_{14} — C_{18})alkylsalicylic acid } 82%m para-substituted

The alkylsalicylic acids obtained were converted into calcium salts with a basicity of 50 and 200%, respectively.

(2) *Starting from para- or ortho-cresol*

Para- or ortho-cresol was alkylated at 200—220°C with a mixture of C_{14}—C_{18} olefins (molar ratio 1.3:1), with 5%w of acid clay as catalyst. The alkylphenols so obtained were converted into the corresponding alkylsalicylic acids by phenation, carboxylation and hydrolysis. In this operation 1 mole of para- or ortho-cresol yielded 0.65 mole of alkylsalicylic acids consisting of practically 100%m of 3-(C_{14}—C_{18}) alkyl - 5 - methylsalicylic acid or 3 - methyl - 5 - (C_{14}—C_{18})alkylsalicylic acid, respectively. The alkylsalicylic acids obtained from para-cresol were converted into calcium salts with a basicity of 200%, those obtained from ortho-cresol were converted into calcium salts with a basicity of 50 and 200%, respectively.

(3) *Starting from phenol*

Phenol was alkylated at 150°C with cetene (molar ratio 1:2.5) with 5%w of acid clay as catalyst. The alkylphenols so obtained were converted into the corresponding alkylsalicylic acids by phenation, carboxylation and hydrolysis. In this operation 1 mole of phenol yielded 0.65 mole of alkylsalicylic acids of the following composition:

12%m 3-cetylsalicylic acid
12%m 5-cetylsalicylic acid } 88%m para-substituted
76%m 3,5-dicetylsalicylic acid

The alkylsalicylic acids obtained were converted into calcium salts with a basicity of 200%m.

The engine performance of these six compounds was investigated by subjecting the salts at a concentration of 0.15%w of calcium in the same lubricating oil as had been used in the model-compound test programme to the same short-duration high-temperature test (lubricant compositions 12—17). For comparison two lubricating oil compositions were prepared from the same lubricating oil which again contained 0.15%w of calcium in the form of calcium alkyl salicylate. One lubricating oil composition was the reference oil already used in the model-compound test programme (reference oil 1), containing a calcium salt with a basicity of 50%, the other one (reference oil 2) contained a calcium salt with a basicity of 200% which had, however, also been derived from the same alkylsalicylic acids as the calcium salt in reference oil 1. Alongside each engine test for the aforesaid six lubricating oil compositions, an engine test with one of the reference oils was carried out. The results of these engine tests have been collected in Table II.

TABLE II

Piston Fouling (10 = clean)

Lubricating oil composition No.	Calcium alkyl salicylate prepared from	Basicity of the calcium salt, %	Degree of piston fouling of compositions 12—17	Reference oil No.	Degree of piston fouling of reference oil	Improvement relative to reference oil
12	salicylic acid	50%	8.3	1	7.4	+ 0.9
13	do.	200%	7.6	2	7.0	+ 0.5
14	para-cresol	200%	7.0	2	6.3	+ 0.7
15	ortho-cresol	50%	7.9	1	7.5	+ 0.4
16	do.	200%	7.6	2	7.2	+ 0.4
17	phenol	200%	7.3	2	6.9	+ 0.4

WHAT WE CLAIM IS:—

1. Lubricant compositions comprising one or more lubricants and one or more salts of polyvalent metals and alkylsalicylic acids, which alkylsalicylic acids contain at least one alkyl group with more than 12 carbon atoms and of which more than 60%m consists of acids containing an alkyl group that is attached to the benzene nucleus in para position relative to the hydroxyl group.

2. Lubricant compositions as claimed in claim 1, wherein the salts of polyvalent metals and alkylsalicylic acids are basic salts.

3. Lubricant compositions as claimed in claim 1 or 2, wherein the salts of polyvalent metals and alkylsalicylic acids are basic salts with a basicity below 250%.

4. Lubricant compositions as claimed in claim 3, wherein the salts of polyvalent metals and alkylsalicylic acids are basic salts with a basicity between 50 and 200%.

5. Lubricant compositions as claimed in any one of the preceding claims, wherein the salts of polyvalent metals and alkylsalicylic acids are salts of divalent metals.

6. Lubricant compositions as claimed in claim 5, wherein the salts of polyvalent metals and alkylsalicylic acids are salts of alkaline earth metals.

7. Lubricant compositions as claimed in

claim 6, wherein the salts of polyvalent metals and alkylsalicylic acids are calcium salts.

8. Lubricant compositions as claimed in any one of the preceding claims, wherein the salts of polyvalent metals and alkylsalicylic acids have been derived from alkylsalicylic acids which contain at least one alkyl group having 14 to 18 carbon atoms.

9. Lubricant compositions as claimed in any one of the preceding claims, wherein the salts of polyvalent metals and alkylsalicylic acids have been derived from alkylsalicylic acids of which more than 70%m consists of acids containing an alkyl group which is attached to the benzene nucleus in para position relative to the hydroxyl group.

10. Lubricant compositions as claimed in any one of the preceding claims, wherein the salts of polyvalent metals and alkylsalicylic acids have been derived from alkylsalicylic acids which have been prepared starting from alkylphenols obtained in the alkylation of phenol, ortho-alkylphenol or para-alkylphenol with one or more olefins having more than 12 carbon atoms to the molecule.

11. Lubricant compositions as claimed in claim 10, wherein the salts of polyvalent metals and alkylsalicylic acids have been derived from alkylsalicylic acids which have been prepared starting from alkylphenols obtained in the alkylation of phenol, ortho-alkylphenol or para-alkylphenol with one or more olefins having more than 12 carbon atoms to the molecule in the presence of an acid clay as alkylation catalyst.

12. Lubricant compositions as claimed in any one of claims 10 and 11, wherein the salts of polyvalent metals and alkylsalicylic acids have been derived from alkylsalicylic acids which have been prepared starting from alkylphenols obtained in the alkylation of ortho- or para-cresol with one or more olefins having more than 12 carbon atoms to the molecule.

13. Lubricant compositions as claimed in any one of claims 10 and 11, wherein the salts of polyvalent metals and alkylsalicylic acids have been derived from alkylsalicylic acids which have been prepared starting from alkylphenols obtained in the alkylation of phenol with one or more olefins having more than 12 carbon atoms to the molecule in a molar ratio of 2 to 4 mole of olefin per mole of phenol, in particular in a molar ratio of 2.5 to 3.0 mole of olefin per mole of phenol.

14. Lubricant compositions as claimed in any one of claims 10, 11 and 12, wherein the salts of polyvalent metals and alkylsalicylic acids have been derived from alkylsalicylic acids which have been prepared starting from alkylphenols obtained in the alkylation of ortho- or para-alkylphenol with one or more olefins having more than 12 carbon atoms to the molecule in a molar ratio of 0.5 to 1.0 mole of olefin per mole of ortho- or para-alkylphenol, in particular in a molar ratio of 0.7 to 0.8 mole of olefin per mole of ortho- or para-alkylphenol.

15. Lubricant compositions as claimed in any one of claims 1—9, wherein the salts of polyvalent metals and alkylsalicylic acids have been derived from alkylsalicylic acids which have been prepared by alkylation of salicylic acid with one or more olefins having more than 12 carbon atoms to the molecule.

16. Lubricant compositions as claimed in claim 15, wherein the salts of polyvalent metals and alkylsalicylic acids have been derived from alkylsalicylic acids which have been prepared by alkylation of salicylic acid with one or more olefins having more than 12 carbon atoms to the molecule in the presence of BF_3 as alkylation catalyst.

17. Lubricant compositions as claimed in any one of claims 15 and 16, wherein the salts of polyvalent metals and alkylsalicylic acids have been derived from alkylsalicylic acids which have been prepared by alkylation of salicylic acid with one or more olefins having more than 12 carbon atoms to the molecule in a molar ratio of 1.5 to 4.0 mole of olefin per mole of salicylic acid, in particular in a molar ratio of 2.0 to 3.0 mole of olefin per mole of salicylic acid.

18. Lubricant compositions as claimed in any one of the preceding claims, wherein the lubricant is a mineral lubricating oil or mixture of mineral lubricating oils.

19. Lubricant compositions as claimed in any one of the preceding claims, which contain 0.01 to 5%w, in particular 0.1 to 1.0%w of polyvalent metal in the form of a salt of a polyvalent metal and an alkylsalicylic acid.

20. Lubricant compositions according to claim 1, substantially as described hereinbefore and with particular reference to the Examples.

21. A process for the preparation of lubricant compositions, characterized in that one or more salts of polyvalent metals and alkylsalicylic acids, which alkylsalicylic acids contain at least one alkyl group with more than 12 carbon atoms and of which more than 60%m consists of acids containing an alkyl group that is attached to the benzene nucleus in para position relative to the hydroxyl group, are incorporated into a lubricant or mixture of lubricants.

22. A process for the lubrication of diesel engines, using a lubricating oil composition as claimed in any one of claims 1—20.

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